Name Key

Photoelectron Spectroscopy

Look at the PES spectrum for hydrogen shown in Figure 1 below.

1. The label on the y-axis is energy, with the units megajoules per mole (MJ/mol). What is depicted on the x-axis below? Elements (by atomic #)

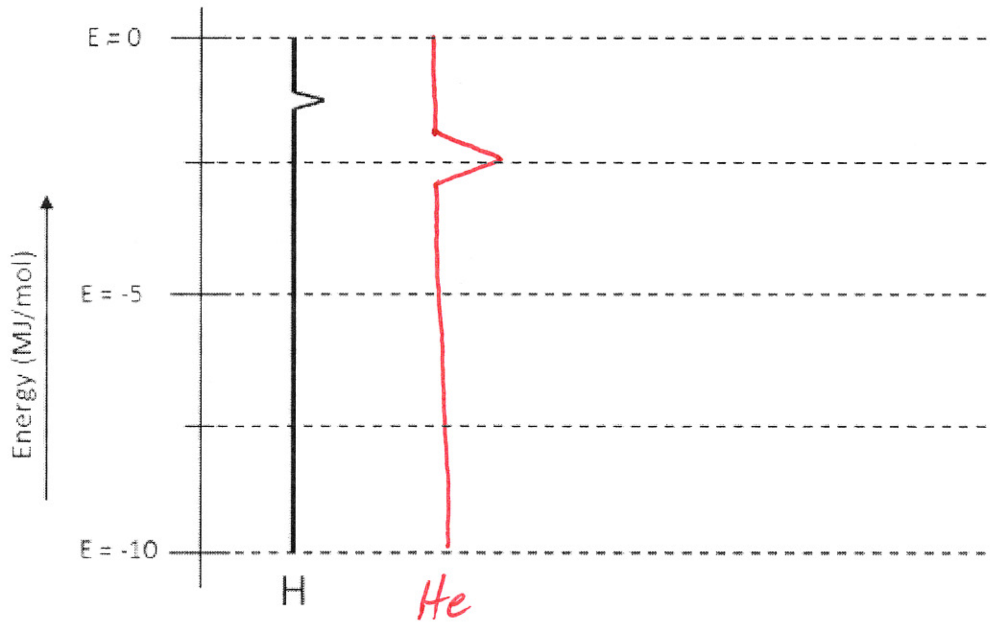

Figure 1

2. Write an equation for this first ionization energy of hydrogen shown in Figure 1? (include energy unit)

$H_{(g)} + 1.2\ \frac{MJ}{mol} \longrightarrow H^+_{(g)} + e^-$

3. Helium is next, but before looking at the photoelectron spectrum, answer the following:

a. how many electrons does helium have in its first shell? 2

b. Will the first ionization energy for helium be greater or less than that of hydrogen? Why?

Greater. Helium has 2 protons, so the e^-s are pulled in closer to the nucleus, so it will take more energy to remove them.

c. **Do NOT look ahead.** Sketch a prediction of what the PES will look like for helium on Figure 1.

4. Look at the PES plot in Figure 2 and compare it to your prediction from the previous question. Describe what you see and the conclusions you can reach. Be sure to comment about the relative energy of the peaks and the number of electrons for each peak for both elements.

It did require more energy than hydrogen (~2 MJ/mol)
The peak is also twice as big because 2 electrons are removed from the same orbital.

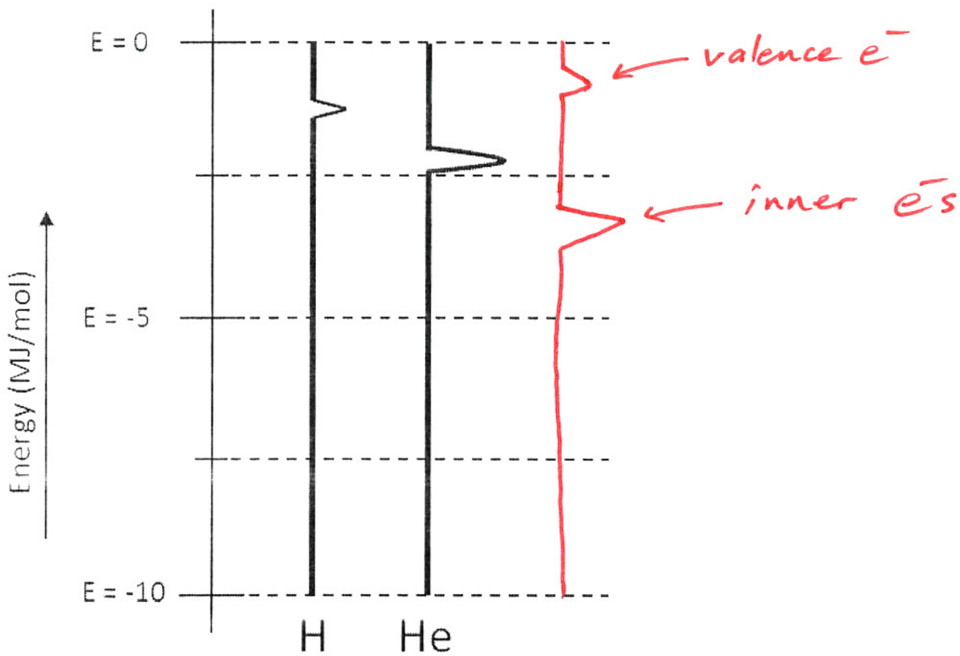

Figure 2

5. The next element is lithium.

a. How many electrons does lithium have, and what shells do those electrons occupy?

3, 2 in the first shell and 1 in the 2nd shell

b. Before looking at the PES for lithium, sketch your prediction of what you believe the spectrum will look like for lithium <u>on Figure 2</u>.

Note: you do not have to predict the exact energies for each electron, but you should be able to make reasonable estimates relative to the previous ionization energies.

6. Examine the PES plot in Figure 3 and compare it to your prediction from the previous question.

a. Label each peak in Figure 3 with the shell occupied by the electrons that correspond to that peak.

b. Describe what you see and the conclusions you can reach. Be sure to comment about the relative energy of the peaks and the number of electrons indicated by each peak in the lithium spectrum.

1. The one valence e^- is farther from the nucleus than hydrogen's so it is easier to remove.

2. The two core electrons were significantly harder to remove than they were for helium.

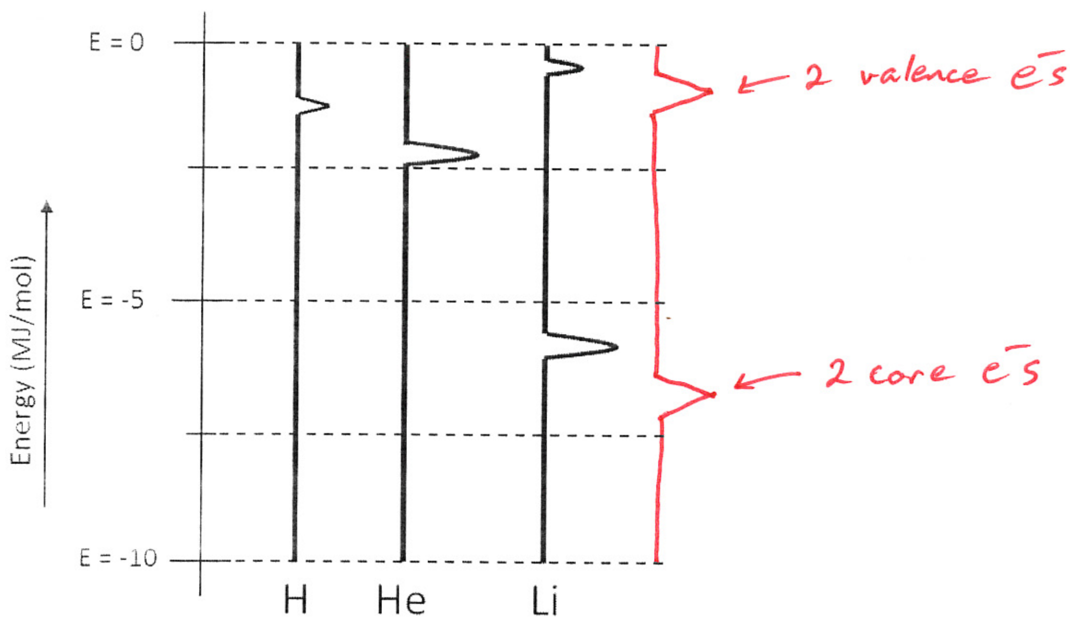

Figure 3

7. The next element is beryllium.

a. How many electrons does beryllium have, and what shells do those electrons occupy?

4 (2 in the 1st shell and 2 in the 2nd)

b. Using Figure 3, sketch what you anticipate the spectrum of beryllium will look like. Think about:

i. how many peaks. 2

ii. the number of electrons for each peak. 2 e^- each

iii. the approximate relative energies of each peak (hint: think about how many protons beryllium has compared to lithium, and if that will make it easier or harder to remove the electrons)

8. Examine Figure 4 below.

a. Label each peak in Figure 4 with the shell occupied by the electrons that correspond to that peak.

b. Based on the number of protons in the nucleus, why are the peaks for beryllium lower on the plot than for lithium?

Be has 1 more proton than Li so the e⁻s are closer to the nucleus and the atomic charge is greater.

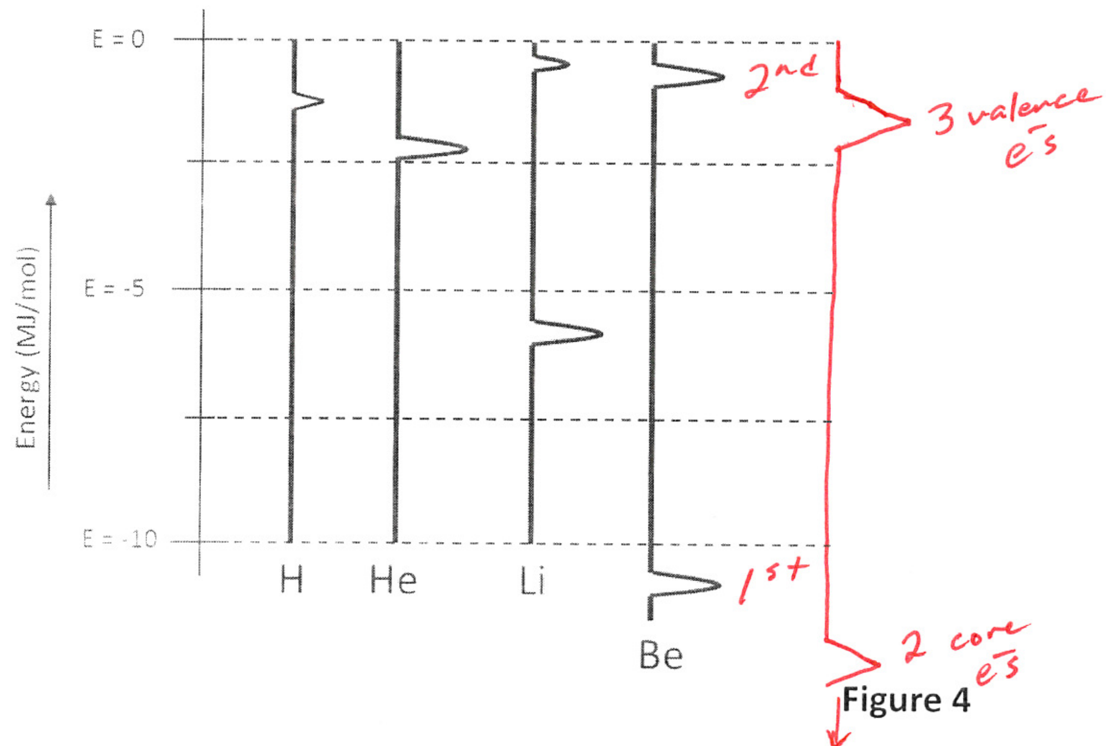

Figure 4

9. The next element is boron.

a. How many electrons does boron have, and what shells do those electrons occupy?

5 (3 in the 2nd level and 2 in the 1st shell)

b. Using Figure 4, sketch what you anticipate the spectrum of boron will look like.

10. Examine Figure 5 below.

a. How can there be three peaks if boron only has electrons in 2 energy levels?

The 2nd energy level has 2 sublevels (s & p); the p-sublevel is at a slightly higher energy state, so it takes a little less energy to remove.

b. Label each peak in the spectrum for boron in Figure 5 below.

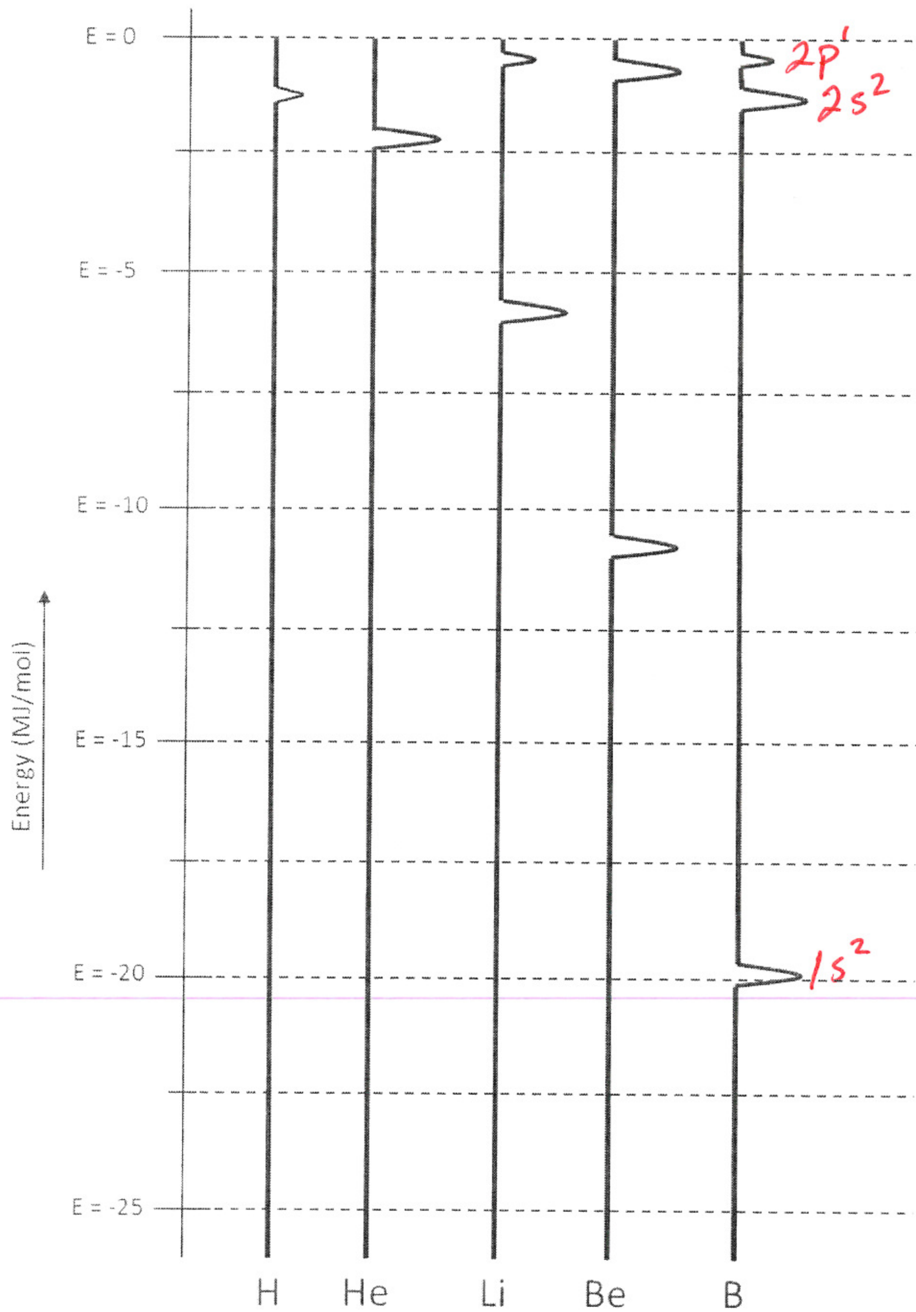

Figure 5

Since the energy gap between energy levels is getting very large, we will start splitting the spectra from this point forward to make them easier to fit on one page. Examine the data in Figure 6 for the spectra of several elements from Period 2 of the periodic table, and then answer the questions on the next page. You might find it helpful to label which shell is represented by each peak.

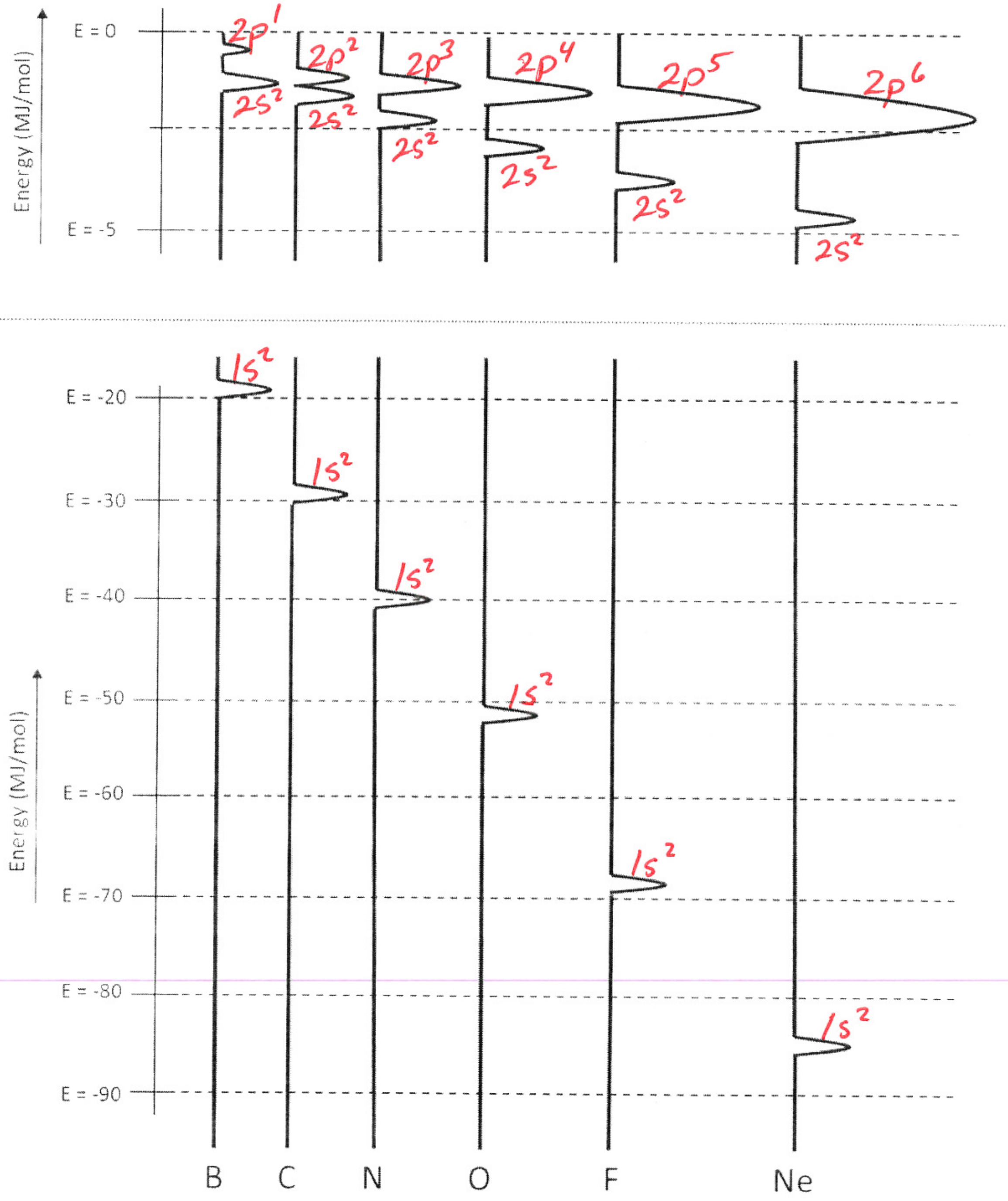

Figure 6

11. Answer the following questions based on the PES plots for hydrogen through neon.

a. After examining the spectra, a student concludes, "The electrons in the second shell all have the same energy." Would you agree or disagree with this statement? Explain.

Disagree. The p-orbital electrons took less energy to remove than those in the s-orbital.

b. How many "subshells" are found in the second shell? __2__ The first shell? __1__

c. Moving systematically through the second period, from lithium to neon:

i. How many electrons are in the first shell for each element in Period 2? __2__

ii. What happens to the energy required to remove an electron in the first shell moving from left to right in the second period? Support your observation with an explanation that references the relevant subatomic particles.

The energy increases moving left to right because each element has one additional proton in the nucleus (greater nuclear charge).

iii. What happens to the energy of the electrons in the outermost shell as you look at the data for elements across Period 2?

The same trend is observed, but the energy difference is less because the valence electrons are farther from the nucleus, so the extra nuclear charge is felt less.

12. Examine the simulated spectra for elements in the third period at the following website - http://www.chem.arizona.edu/chemt/Flash/photoelectron.html. Click on the element's icon on the periodic table to view the PES spectrum. You will note that energy is on the x-axis here.

a. Are there any surprises in the data? Yes, sulfur requires <u>less</u> energy to remove a 3-p electron than phosphorus even though it has a greater nuclear charge.

b. Briefly summarize your observations, and provide an explanation based on subatomic particles, energy shells, and subshells.

sulfurs orbital diagram for 3p looks like this: | ↑↓ | ↑ | ↑ |
The last electron fills in an orbital that is already occupied, so the extra repulsion is stronger than the attraction to the extra proton in the nucleus.

13. Look at the PES plots for potassium, calcium, and scandium.

a. Something very interesting happens in the spectrum for scandium that we have not seen for any element prior to scandium. Explain.

The extra electron requires MORE energy to remove than the previous 2 electrons.

- up to this point each additional sublevel required less energy than the one before it.

b. If one electron is removed from scandium, which electron requires the least amount of energy to remove? (identify the shell and subshell)

It takes the least energy to remove an electron from the 4s sublevel because they are valence electrons.